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Synthetic Approach to Controlled Assembly of Metal Nanoparticles.

**So-Jung Park
Ewha University-Industry Collaboration Foundation**

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Final Report**

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Abstract:

The aim of this one-year project is to develop synthetic methods to form well-defined colloidal assemblies of metal nanoparticles and to understand their unique optical properties focusing on magnetic resonance scattering and surface enhanced Raman scattering (SERS). Our synthetic approach is based on the templated surfactant-assisted seed growth method, where polymer particles decorated with small metal nanoparticles are used as seed-decorated templates to grow metal nanoparticles of varying sizes and shapes. Of particular interest in this study is closely packed gold nanobeads assembled on a polymer core, which is termed raspberry-like metamolecules (raspberry-MM) due to their strong magnetic resonances. Here, we first report surprisingly weak distance dependence in Raman enhancement from the raspberry-like gold nanoparticles. Due to the abundant “built-in” hot spots between adjacent gold nanobeads, bright and uniform Raman signals were observed from isolated single raspberry-MMs. Interestingly, dimers of raspberry-MMs also showed highly reproducible Raman signals, indicating that the dimer SERS signal is not strongly dependent on the nanoparticle separation. Finite-difference time-domain (FDTD) modeling shows that a strong hot spot is created at the dimer gap, as expected. However, since there are many more built-in hot spots in each raspberry-MM, the contribution of the dimer gap hot spot to the total Raman enhancement remains low even for 2 nm separation, which explains the observed weak distance dependence. This result is in stark contrast with many previous SERS studies on nanoparticle dimers and clusters, and provides an important guideline on how to design bright and highly reproducible Raman substrates. Secondly, we have developed a synthetic method to prepare “silver” raspberry-type nanoparticles. Silver particles possess higher extinction cross section than gold particles, and show surface plasmon resonance (SPR) peaks blue-shifted from those of gold particles. Therefore, this capability allows for the fabrication of raspberry-MMs with enhanced magnetic resonances in the visible region.

Major Findings

Part 1. Unusual Weak Interparticle-Distance Dependence in Raman Enhancement from Nanoparticle Dimers

This work has been published in *J. Phys. Chem. C* and was featured on the journal cover, as cited below in the list of publications. Figure 1 presents the key result of this study showing unusual distance-insensitive SERS from raspberry-MMs. A copy of this paper is also provided with this report as an appendix.

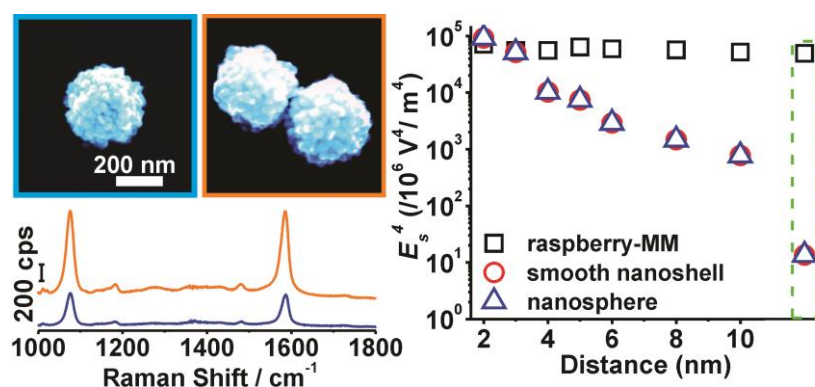


Figure 1. (left) SEM images and SERS spectra of raspberry-MM monomers and dimers. (right) Distance dependence of calculated SERS intensity for three different nanostructures. The points in the green box indicate the intensities of isolated nanoparticles.

Part 2. Synthesis and Properties of Silver Raspberry-MMs

Introduction

It has been proposed that sub-wavelength metal nanoparticles arranged into a two dimensional ring structure or three-dimensional clusters can support magnetic resonances at optical frequencies.[1] This unusual property of metal nanoparticle clusters, which are often termed “metamolecules”, has stimulated new exciting applications such as plasmonic cloaking, superlenses, and enhanced nonlinear optical properties.[2-4] In our previous work, we have developed a synthetic approach to prepare isotropic shell-type gold nanoparticle clusters exhibiting strong magnetic resonances.[5] Our synthetic method, which is based on templated surfactant-assisted seed-growth method, allows for an in-situ formation and assembly of gold nanobeads and yields raspberry-like structures where gold nanobeads are closely packed within a few nanometers of separation. Our prior result indicated that raspberry-type assemblies of gold nanoparticles prepared by the templated surfactant assisted seed growth method show unprecedented strong magnetic resonances. In this work, we developed a synthetic method to prepare silver raspberry-MM to enhance their scattering properties and to expand the wavelength range into the visible region.

Results and Discussion

Silver raspberry-MM was synthesized based on the templated seed growth method through a judicious choice of reductants and additives. Simple replacement of gold precursors with silver precursors in the synthesis of gold raspberry-MMs did not yield well-defined raspberry-type particles. In our typical synthesis, seed-decorated PS templates were synthesized by the reduction of silver ions in the presence of polystyrene (PS) template. Then, the seed solution was mixed with a growth solution containing sodium citrate and silver nitrate, followed by the quick injection of fresh n-propyl gallate (PG) solution (Figure 2A). Figure 2B-F presents SEM images of silver nanostructures synthesized using different amounts of seed at a constant volume of growth solution. At a high volume of seeds (V_{seed}), a discontinuous layer of silver nanoparticles were formed on the surface of the PS template (Figure 2B). This structure exhibited an extinction peak at 450 nm (Figure 2G, black curve). With decreasing V_{seed} , the silver nanoparticles gradually grow bigger, filling the surface of PS templates (Figure 2D-F). These particles show multiple extinction peaks (Figure 2G, blue curve) with new shoulder peaks at longer wavelengths presumably from the coupling between adjacent particles.

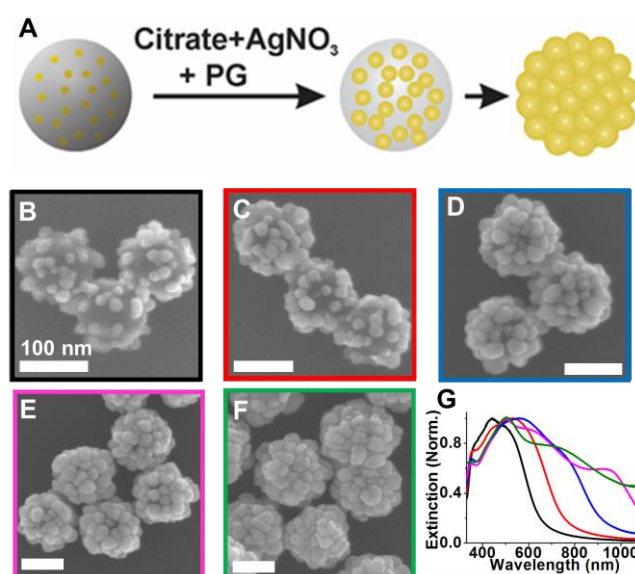


Figure 2. (A) Pictorial description of the growth procedure of silver raspberry-MMs. (B-F) SEM images of nanoshells synthesized with varying volumes of seed-decorated polymer beads solution for 8 mL of growth solution. The volume of seed solution was 256 μL (B), 128 μL (C), 64 μL (D), 32 μL (E) and 16 μL (F). (G) Normalized extinction spectra of synthesized particles (B: black, C: red, D: blue, E: magenta, F: green).

In order to confirm that the silver nanobeads composing the raspberry-MMs maintain the discrete nature, synthesized silver raspberry-MMs were treated with thiolated polyethylene glycol (PEG) and incubated in ethanol. This procedure causes swelling of PEG and partial disassembly of silver nanobeads. TEM images in Figure 3 show individual silver nanobeads from raspberry-MM particles, confirming that silver beads are not fused together on PS templates. Therefore, the synthesized particles meet the two important requirements for supporting magnetic resonances. We are currently investigating the optical properties of silver raspberry-MMs, and expect that this study will lead to better understanding on what affects the

unique magnetic resonance scattering of metal nanoparticle assemblies.

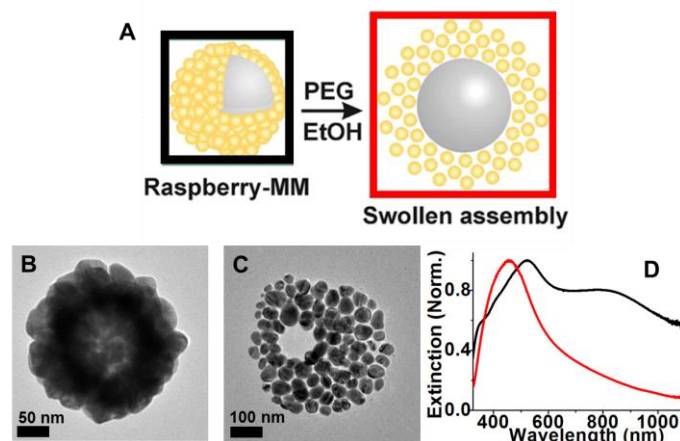


Figure 3. (A) Schematic description of the disassembly procedure used to separate silver nanobeads from PS templates. (B) A TEM image of a typical silver raspberry MMs. (C) A TEM image of PEG-grafted silver raspberry MMs swelled in ethanol for 2 h. (D) UV-vis spectra of the silver raspberry MMs (black) and swollen assemblies (red).

References

1. Alù, A.; Engheta, N. The quest for magnetic plasmons at optical frequencies. *Opt. Express* **2009**, *17*, 5723-5730.
2. Chen, P.-Y.; Soric, J.; Alù, A. Invisibility and Cloaking Based on Scattering Cancellation. *Adv. Mater.* **2012**, *24*, 281-304.
3. Argyropoulos, C.; Chen, P.-Y.; Monticone, F.; D'Aguanno, G.; Alù, A. Nonlinear Plasmonic Cloaks to Realize Giant All-Optical Scattering Switching. *Phys. Rev. Lett.* **2012**, *108*, 263905.
4. Casse, B. D. F.; Lu, W. T.; Huang, Y. J.; Gultepe, E.; Menon, L.; Sridhar, S. Super-resolution imaging using a three-dimensional metamaterials nanolens. *Appl. Phys. Lett.* **2010**, *96*, 023114.
5. Qian, Z.; Hastings, S. P.; Li, C.; Edward, B.; McGinn, C. K.; Engheta, N.; Fakhraai, Z.; Park, S.-J. Raspberry-like Metamolecules Exhibiting Strong Magnetic Resonances. *ACS Nano* **2015**, *9*, 1263–1270.

List of Publications resulted from AOARD supported project:

I. Papers published in peer-reviewed journals,

1. Qian, Z.; Li, C.; Fakhraai, Z.*; Park, S.-J.* "Unusual Weak Interparticle Distance Dependence in Raman Enhancement from Nanoparticle Dimers" *J. Phys. Chem. C*, **120**, 1824-1830 (**2016**). [Featured on the Journal Cover]

II. Conference presentations,

1. S.-J Park, Z. Qian, C. Li, Z. Fakhraai, Raspberry-like Metamolecules: Strong

Magnetic Resonances and Distance-insensitive SERS, Invited talk, 117th KCS meeting, Ilsan, Korea, April 20-22, 2016.

2. S. Lee, H. Song, S.-J Park, Controlling the Shape and Assembly of Metal Nanoparticles. Marie Skłodowska-Curie Conference, Poster presentation, Seoul, Korea, May 24th 2016.
3. S. Lee, H. Song, S.-J Park, Shape-controlled Synthesis and Assembly of Metal Nanoparticles, Poster presentation, NANO KOREA 2016 Symposium: Nanotechnology, the Great Beginning, Ilsan, Korea, July 13-15, 2016.